

# PATENT SPECIFICATION

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- (21) Application No. 39569/76 (22) Filed 23 Sept. 1976  
 (31) Convention Application No. 623 417  
 (32) Filed 17 Oct. 1975 in  
 (33) United States of America (US)  
 (44) Complete Specification published 1 March 1978  
 (51) INT CL<sup>2</sup> C22B 1/04, 34/10  
 (52) Index at acceptance

C1N 212 213 251 261 276 337 347 34X 35Y 366 367 406 407  
 408 410 414 422 42Y 511 524 535 536 543 580 592  
 593 594 597 617 630 63X 64X 666 684



## (54) ILMENITE OXIDATION IN A CARBON-CONTAINING FLUIDIZED BED

(71) We, TITANIUM TECHNOLOGY (AUSTRALIA) LIMITED, a company incorporated in the State of New South Wales, of 12th Floor, Lend Lease House, 47 Macquarie Street, Sydney, New South Wales 2000, Australia, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to the beneficiation of minerals and more particularly to the oxidation of titaniferous ores such as ilmenite to facilitate high temperature selective removal of iron values in said ores by leaching or chlorination process.

Ilmenite oxidation is a rapid and easy process which takes place at temperatures from 600°C. and higher in an oxygen containing atmosphere. The product of an ilmenite oxidation may vary depending upon the nature of the ilmenite and the temperature of oxidation. There is a tendency to transform the material to pseudobrookite at temperatures of 900°C. and over as taught by Robinson et al in U.S. 3,875,286 and Fukushima et al in U.S. 3,803,287. Fukushima says, 'the oxidation-roasting weakens the reactivity of titanium in ilmenite with chlorine to accelerate the preferential chlorination of iron and at the same time improves the separation of iron in the course of electrostatic dressing.' In Robinson a preoxidation step has been taught followed by a reduction step to improve leaching beneficiation using, for example, hydrochloric acid which contains some ferrous chloride to aid the leaching process.

Robinson does not claim the oxidation conditions as part of his invention. Both Robinson and Fukushima follow the oxidation by a reduction in an oxygen deficient atmosphere.

In high temperature chlorination beneficiation of beach and ilmenite, it is necessary to preheat the ilmenite in order to drive off hydrogen present not only as water but as part of hydroxyls absorbed on the extensive ore surface. The removal of hydrogen is required in order to prevent chlorine losses to hydrogen chloride at a high temperature of the beneficiation reactor.

Another and equally important reason for preheating the ilmenite is to maintain the heat balance for the high temperature chlorination beneficiation since high temperatures are desirable for desired rates of reaction and volatilization. Therefore it is convenient in beneficiation by high temperature chlorination to preheat the ilmenite to temperatures in excess of 600°C.

We have discovered that it is possible to combine both oxidation and preheating of ilmenite by passing air or oxygen through a mixture of ore and particulate carbon wherein the combustion of carbon over a range of temperatures provides the heat required yet unexpectedly the presence of carbon does not prevent oxidation of the ore. Our process is particularly desirable since it saves natural gas and substitutes cheaper coke which is presently a more available fuel.

This invention is directed to a process for heating and oxidizing a titaniferous ore to remove water and hydroxyl groups from the ore and at the same time oxidize the ore to a form more amenable to beneficiation by the selective removal of iron values from said ore by contacting the ore mixed with particulate carbon, preferably under fluidizing conditions, at temperatures of 600 to 1080°C. with air, oxygen or oxygen enriched air preferably for a period of time of 0.1 to 3 hours or longer.

In a preferred embodiment the carbon is petroleum carbon and the time is 0.5 to 1.5 hours and the temperature is 650 to 950°C. Most preferably the air, oxygen or oxygen enriched air is contacted with the ore for 0.1 to 3 hours at a velocity of 0.5 ft./sec. The process can be carried out in a fluidised bed reactor preferably continuously.

The heat oxidized product is useful as a raw material for the production of titanium dioxide pigments. We have found that such a coke-ilmenite bed can be operated under stable conditions in the range of temperature needed for drying and dehydroxylating weathered ilmenites and provide preheated ore at a suitable temperature to meet the heat balance needs of the beneficiator reactor.

Stability of operation of a fluidized carbon bed is more easily achieved in the high temperature region where the carbon combustion reaction is diffusion controlled. The more than four fold difference in energy of activation between the kinetic and diffusion controlled regime of carbon combustion improves stability.

Although increased bed depth can be used to counter decreased reactivity there is a disadvantage to bed depth in that it increases holding time. We have found that the benefits of ilmenite oxidation can be countered by long holding time which allows crystal changes that reduce the beneficiation activity of an oxidized ore. The preferred bed depth is 0.5 to 3 ft.; however the bed depth can be deeper, i.e. 3 to 6 ft.

Our invention operates in the high reactivity region to allow bed depth and holding time to be minimized while still yielding substantial oxidation. By controlling the ratio of geometric surface areas and by keeping temperature within suitable ranges, both combustion, ore oxidation and preheater stability can be maintained.

The unstable region of temperature will depend upon the activity of the carbon surface. Petroleum coke with its inert qualities is well suited to beneficiation reactors. Ignition temperature is high and the stable region of the bed operation with air lies above 550°C. and coincides nicely with the above mentioned requirements for ore preheating to temperatures of 600°C. and above.

By using a fluidized ilmenite bed, particles can travel from the zone above the oxygen down into a zone where they can be oxidized for a portion of the time spent in the bed. The production of carbon monoxide by carbon surface reaction with oxygen is followed by the secondary conversion to carbon dioxide in the gas phase and temperatures below 1000°C. will yield substantially all carbon dioxide and thus will not hinder the ilmenite oxidation by subsequent reduction by CO.

In the following Examples mesh sizes are British Standard Mesh.

#### EXAMPLE 1

A 1" diameter quartz fluidized bed reactor externally heated was charged with 20 g of ilmenite and 4 g of coke. The properties are given in Table I. Table II gives data from 10 minute runs for three temperatures.

TABLE I

#### SOLID REACTANT PROPERTIES

Ilmenite:	Murphyores (East Coast Australian),	20 g
	Natural State $\text{TiO}_2$	— 54.5%, by weight
	FeO	— 20.9%, by weight
	$\text{Fe}_2\text{O}_3$	— 20.8%, by weight
Coke:	Great Lakes Carbon Co. calcined petroleum coke. 4 g. Selected fraction 30 x 44 mesh containing 1% S.	
Air:	52 mmols/min for 10 minutes.	

TABLE II

Laboratory Fluidized Bed Air Oxidation of an Ilmenite-Coke Mixture

TEMPERATURE	ANALYSIS <sup>+</sup>		COKE OUT <sup>++</sup>	MMOLS AIR* Consumed to oxidise		
	°C	%Fe <sup>+</sup>	%Fe <sup>++</sup>	grams	Coke (1)	Ilmenite (2) Total
650°	30,80	3,28	3,1381	342	11,0	453
750°	30,71	3,06	3,017	390	112,8	502,8
850°	30,93	2,51	3,007	394	117,5	511,5

\*Calculated from carbon loss and iron oxidation.

Notes:

<sup>+</sup> %Fe<sup>+</sup> and %Fe<sup>++</sup> refer respectively to total iron and iron in the ferrous state — elemental iron in each case.<sup>++</sup> Weight of coke remaining after run.(1) MMOLS air required to convert coke to CO<sub>2</sub>.

(2) MMOLS air required to convert ferrous iron to ferric iron.

This example shows that the ilmenite can be substantially oxidized in the presence of carbon at temperatures above the kinetic limiting range and that although the air was nearly all consumed in combustion and oxidation, a constant fraction, i.e. 23%, went to oxidize the ilmenite at 750°C. and above.

Some ilmenite grains are more difficult to oxidize than others and it seems likely that the residual ferrous is all in the more difficultly oxidized grains. Thus the easily oxidized ilmenite was quickly converted.

## EXAMPLE II

A fluidized bed reactor 5 ft. 6 in. ID, refractory lined with a multipoint gas distributor was operated with an ore-coke mixture of 10" static bed depth. Table III gives a series of analyses of samples taken from the bed which was cycled between reduced and oxidized conditions as indicated by the time elapsed. Reduction took place while the bed was static, oxidation while the bed was being heated up at a superficial gas velocity of about 0.8 ft./sec. On each cycle the bed was brought to 950°C. before being set down.

TABLE III

Temp.	Sample	Time	% Coke (1)	Cycle	%Fe <sup>++</sup> (2)	Activity % Min. (3)
950°	1		6,23	Initial	72,88	83,6
865	2	64 min.	9,90	Red.	84,31	84,31
950	3	36 „	9,84	Oxid.	75,25	97,8
890	4	54 „	8,09	Red.	78,53	98
950	5	26 „	7,72	Oxid.	50,66	139,4
835	6	137 „	7,01	Red.	86,71	57,5
950	7	50 „	6,40	Oxid.	42,48	92
710	8	609 „	5,15	Red.	90,27	59,8
950	9	65 „	2,91	Oxid.	22,93	128

Notes:

(1) % in ilmenite/coke mixture

(2) % of iron in ferrous state as % total iron in ilmenite

(3) seed definition after Table IV

The bed was refluidized with nitrogen and sampled after reduction periods. On heat up cycles oxygen enriched air was used with a maximum of 30% oxygen. Coke was added after the initial sample.

To illustrate the deleterious effect of excessive holding time example III is presented.

#### EXAMPLE III

Laboratory oxidation by reaction of the oxidized ilmenite with  $\text{TiCl}_4$  was accomplished by a 1" fluidized bed on 20 g samples of Murphys ores ilmenite using 52MMOL/mm of air for oxidation without carbon being present. It was found that oxidation for long periods of time could be completed but the product possessed low replacement rates when compared to natural or rapidly oxidized ore. Table IV gives results of slow oxidations and the ore activities compared with rapid oxidation rates.

TABLE IV

Effect of Time at Temperature on Beneficiation Activities of Oxidized Beach Sand Ilmenite

Time	Oxidation Temperature	Iron Oxide % Ferric	Activity* %/min
0 hrs.	Natural Murphys ores (no oxidising treatment)	50%	140,0
16 hrs.	650°C.	100%	36,5
5 hrs.	900°C.	100%	57,5
30 min.	900°C.	100%	140,0

\*Iron oxide replacement with  $\text{TiCl}_4$  to form internal  $\text{TiO}_2$  and volatilize iron chlorides at 1000°C.

Activities given in Tables III and IV are replacement rates taken from the slope of a semi-log plot of log (grams Fe remaining) vs. time. The same laboratory reactor as was used in Example I is charged with 10 grams of ilmenite (without carbon) and fluidized at a 0,5 ft/sec. velocity using 26 mmols/min. each of  $\text{TiCl}_4$  and nitrogen. Samples were taken at various time intervals.

It is apparent from the activities shown in Table III that the activities can vary up and down not only with the oxidation state but with holding time at high temperatures.

Therefore, to practise our invention under preferred conditions, the fluidized bed wherein the ore and carbon are preheated, dried and oxidized, should be designed and operated within the following limits:

Retention time less than 3 hours  
Carbon surface area less than 30 ft<sup>2</sup>/lb.  
Gas velocity 0.3—1.5'/sec.  
Temperature 650—950°C.

Carbon-air ignition temperature above 450°C.

Consideration should be given to the type of ilmenite particle to be oxidized. Massive ilmenites such as Tellnes ores have to be oxidized at higher temperatures than highly weathered beach sands, although for complete oxidation beach sands which contain small amounts of unweathered ilmenite will require higher temperatures or longer oxidation exposure time.

#### WHAT WE CLAIM IS:—

1. A process for oxidizing a titaniferous ore comprising contacting the ore mixed with 5 to 35% by weight of a particulate carbon with air, oxygen or oxygen enriched air at a temperature of 600 to 1080°C.

2. The process of Claim 1 wherein air, oxygen, or oxygen enriched air is contacted with the ore for a period of time of 0,1 to 3 hours.

3. The process of Claim 2 wherein the carbon is a petroleum coke and the time is 0,5 to 1,5 hours and the temperature is 650 to 950°C.

4. The process of Claim 1 wherein the process is conducted in a fluidized bed reactor.

5. The process of Claim 4 wherein the air, oxygen or oxygen enriched air is contacted with the ore for 0, 1 to 3 hours at a velocity of 0,5 ft/sec.

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6. The process of Claim 4 conducted continuously.

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7. A process for oxidizing a titaniferous ore as claimed in Claim 1 substantially as hereinbefore described.

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Printed for Her Majesty's Stationery Office by the Courier Press, Leamington Spa, 1978.  
Published by the Patent Office, 25 Southampton Buildings, London, WC2A 1AY, from  
which copies may be obtained.